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MEMORANDUM FOR P3:20

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FROM:

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SUBJECT:

CHEMISTRY AND QUANTITY OF BRINES THAT SHOULD BE CONSIDERED
IN WASTE PACKAGE STUDIES FOR SALT SITES

In response to questions which arose at the recent NRC/DOE salt repository project (SRP) meeting concerning the quantity and chemistry of brines which may contact the waste package I have done a brief literature review and I obtained new information on WIPP brines. Substantial differences exist between the concepts, data and models presented in the SRPO review and the literature. In this note I wish to outline major discrepancies which may be important to waste package performance.

1. Quantity of Brine and Mode of Brine Migration

The DOE model of brine migration which the DOE is using to predict the quantity of brine available for interaction with the waste package is that of Jenks and Claiborne (1981). The Jenks and Claiborne model has been reviewed by Roedder. Roedder (1984), stated "However, Roedder and Chou (1982) showed that because the values used by Jenks and Claiborne for the major input parameters were either nonconservative selected values, or were based on inadequate data, their calculations were not sufficiently conservative. Truly conservative estimates should be larger, perhaps by as much as two orders of magnitude, than those made by Jenks and Claiborne."

The single crystal brine migration tests used extensively by DOE are not relevant to migration along grain boundaries. According to Roedder (1984) "Small scale experimental studies (Roedder and Belkin, 1980a) show that on intersecting a grain boundary, most fluid inclusions do not cross, but

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PDR WASTE
WM-16 PDR

1306

instead leak their fluid into the interface. How the fluid will then behave involves too many variables to permit meaningful quantitative modelling at this time, and the interpretation of some larger scale laboratory experiments is ambiguous (Lambert, 1980; Roedder and Belkin, 1980a). Full scale, rather long term experiments at the selected site itself, carefully planned to avoid ambiguity in interpretation of the data obtained, seem to present the only likely solution."

In-situ brine migration data cited in the SRP meeting, from the Asse mine in domal salt in Germany are being measured under conditions which are vastly different from those expected at a bedded salt site. According to Roedder (1984), "Bedded salt may contain several percent total H_2O (Roedder and Belkin, 1979a), but some dome salts have only ~30 ppm H_2O (Knauth and Kumar, 1981)." Moreover domal salt is high purity NaCl which has been completely recrystallized whereas bedded salt is relatively impure and only partially recrystallized. The most relevant available data set for brine migration at the SRP bedded salt sites is that being developed at the WIPP site which is located in bedded salt. At the WIPP site holes drilled in the floor of drifts were observed to fill with brine and weeps were sampled in the walls of the drifts (Stein and Krumhansl, 1985). These observations are consistent with the hypothesis that substantial brine migration occurs along salt grain boundaries in the absence of the thermal brine migration mechanism proposed in Jenks and Claiborne (1981). Clearly, the Jenks and Claiborne model is not conservative for predicting the volume of brine available for interaction with the waste package in bedded salt. The heater experiments at WIPP should be closely followed by the NRC so that we can design our research and technical assistance efforts properly. In the absence of those data I would suggest that Roedder's 1985 estimate, that conservative estimates of brine quantities should be as much as two orders of magnitude greater than the estimate of 250 ml/yr or less made by Jenks and Claiborne (1981), should be used in NRC work.

2. Boiling of Brine

In the NRC/DOE meeting the suggestion was put forth that brines that moved in the vicinity of the waste package would tend to boil off and therefore would not accumulate around the waste package. However, the boiling point of brines, especially Mg Cl rich bitters, increases with the concentration of solute. According to Stewart and Potter (1979), "If H_2O is lost from less concentrated bitters they will become more concentrated, may cease to boil, and become stable even at elevated repository temperatures." Therefore, extremely concentrated brines which do not boil at repository temperatures could exist in contact with the

waste package. Moreover, "The dense bitterns have pH's near 4 to 5 at room temperature, and become more acidic by hydrolysis at higher temperature. The pH at 200°C is approximately 2, with Mg-rich bitterns being more acid than Ca-rich bitterns," (Stewart and Potter, 1979). Therefore, if the waste package is in contact with brines that are allowed to boil, solute concentrations will be increased and pH decreased to the point that at 200°C, for a 3/1 molar ratio Mg/Ca solution, a 20 molar Mg + Ca concentration could be reached, although at some point crystalline hydrates will form (Stewart and Potter, 1979). Waste package testing will need to be done for concentrations perhaps as high as 20 molar Mg + Ca if boiling may occur. The possibility exists that water vapor produced by boiling would migrate a short distance, precipitate, then migrate as liquid towards the waste package while dissolving K, Mg and Ca preferentially from the salt. Thus, brine boiling might cause a small decrease in brine volume while substantially concentrating the brine.

3. Chemistry of Brines in Salt

Four groups of brine chemistries were observed by Stein and Krumhansl at WIPP. Two groups of fluid inclusions were identified by chemistry, and brines collected from the walls of rooms were observed to differ moderately in chemistry from samples collected from holes in the floor (Stein and Krumhansl, 1985). Table 5 (enclosed) from Stein and Krumhansl (1985), summarizes the WIPP brine chemistry data. The wide variation in observed brine chemistries is probably the result of both different origins of the water and different mineral/brine reactions. Stein and Krumhansl (1985) identified three likely sources of water. First, seawater inclusions may have been trapped in the process of salt formation. Second, gypsum may have dehydrated. Third, clays may have dewatered. Post-depositional reactions that may have occurred include the alteration of calcium sulfate to polyhalite and calcium carbonate to magnesite and uptake of Mg in preference to K by clay minerals (Stein and Krumhansl, 1985). Fisher (1984) found that "The fluids present and trapped in individual Palo Duro salt inclusions (even adjacent inclusions) differ drastically in chemical composition among themselves."

The Palo Duro Basin observations of highly variable chemistry appear to be consistent with the WIPP observations. Although differences in chemistries exist between the two sites, for example the Palo Duro Basin seems to have had more limestone initially deposited in the host rock and therefore more Ca may be found in the Palo Duro brines, many of the same chemical reactions appear to have occurred at both sites.

In the NRC/DOE meeting the argument was made that, if large bodies of water such as brine pools would by some unanticipated means come in contact with the waste package, these brines would be dissolution brines which would be very low in K and Mg, similar to WIPP brine B. Although the WIPP brine B is saturated with respect to NaCl it is not saturated with respect to KCl, MgCl or CaCl. Therefore any dissolution brine moving through salt would tend to slowly enrich in K, Mg, and Ca. Because of the limited amount of Mg present in the salt, the Mg concentrations could probably never reach the 40 parts per thousand level present in WIPP fluid inclusions, but Mg concentrations might be significantly elevated above the 0.008 parts per thousand level of WIPP brine B.

4. Conclusion

In conclusion, the mobility of intergranular brines must be considered in addition to fluid inclusions and a wide range of brine chemistries should be used in waste package testing for salt repositories.



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Table 5. Summary of Brine Data (in ppt)

	Ca	Mg	K	Na	Cl	Br	SO ₄
Group I	0.23	42.8	7.2	32.3	165	2.8	18.4
Group II	0.39	23.6	9.8	67.8	170.3	1.27	21.8
Floor smpls.	0.28	20.7	13.06	57.7	166.6	1.4	17.7
Weeps ¹	0.32	21.3	17.0	73.9	181.0	.98	17.8
Salado ²	0.61	45.5	29.8	34.8	204.1	.38	2.8
Rustler ²	0.74	0.25	0.15	11.5	7.83	—	3.01
Castile ²	0.24	0.64	2.13	65.8	103.8	0.1	9.3
Brine A ³	0.5	29.2	25.0	35.0	158.3	0.3	2.9
Brine B ³	0.75	0.008	0.01	95.8	145.8	0.3	2.9

¹Weep data for Ca, Mg, K, Na, and Cl include averages of only one set of samples (those in Table 2). Br and SO₄ data are taken from a preliminary set of samples which were analyzed for Br and SO₄ but are not reported here due to apparent contamination with halite.

²From Lambert, 1978

³From Molecke, 1983